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CYCLIC POLYOLEFINS. XXV. CYCLO["]OCTANEDIOLS.
MOLECULAR REARRANGEMENT OF CYCLO["]OCTENE OXIDE ON SOLVOLYSIS.

by

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Cyclic Polyolefins. XXV. Cyclooctanediols.

Molecular Rearrangement of Cyclooctene Oxide on Solvolysis¹

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- (1) Supported in part by the Office of Naval Research under Contract N5ori-07822, Project Designation NR-055-96.
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By Arthur C. Cope, Stuart W. Fenton² and Claude F. Spencer³

- (2) Arthur D. Little Postdoctorate Fellow, 1950-1951.
- (3) Abstracted in part from the Ph.D. dissertation of Claude F. Spencer, Massachusetts Institute of Technology, June, 1950.
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Hydroxylation of cis-cyclooctene with performic acid, and hydrolysis or solvolysis with formic acid of cis-cyclooctene oxide, have been found to yield 1,4-cyclooctanediol in larger amount than the expected product, trans-1,2-cyclooctanediol. The structure of 1,4-cyclooctanediol was established by conversion to cyclooctane through the diacetate and cyclooctadiene, and by Oppenauer oxidation to 1,4-cyclooctanediols, which by an intramolecular aldol condensation formed the known ketone, bicyclo[3.3.0]-1(5)-octan-2-one. The molecular rearrangement resulting in formation of the 1,4-glycol is

interpreted as a chemical "transannular effect" which permits participation in the solvolysis of the epoxide by a carbon-hydrogen bond that is sterically adjacent because of its location across the compact eight-membered ring.

cis-1,2-Cyclooctanediol and the eight-membered cyclic acyloin suberoin have been prepared and characterized.

Before cyclooctene from the partial hydrogenation of cyclooctatetraene⁴ was available as an intermediate for the synthesis of

- (4) W. Reppe, O. Schlichting, K. Klager and T. Toepel, Ann., 560, 1 (1948).
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other eight-membered ring compounds such as 1,3-cyclooctadiene,⁵ an

- (5) A. C. Cope and L. L. Estes, Jr., This Journal, 72, 1128 (1950).
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investigation of the preparation of 1,2-cyclooctanediols (and 1,3-cyclooctadiene) from the cyclic acyloin suberoin was undertaken. When cyclooctene became available, it was converted into cis- and trans-1,2-cyclooctanediols. This phase of the work led to discovery of an unusual rearrangement that occurs during the solvolysis of cyclooctene oxide.

The acyloin condensation of dimethyl suberate, under conditions similar to those used for the preparation of other macrocyclic acyloins,⁶ formed suberoin in 37% yield as a colorless, low-melting solid.

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- (6) J. L. Hanesley, U. S. Patent 2,228,268 (Jan. 14, 1941); C.A., 35, 2534 (1941); V. Prelog, L. Frankiel, M. Kobolt and P. Barman, *Helvetica Chimica Acta*, 30, 1741 (1947); M. Stoll and J. Hulstkamp, *ibid.*, 30, 1815 (1947); M. Stoll and A. Rouvé, *ibid.*, 30, 1822 (1947).
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Hydrogenation of suberoin in the presence of Raney nickel yielded a mixture of glycols, from which cis-1,2-cyclooctanediol was separated by crystallization as leaflets melting at 77.5-79°. Chromatography on alumina of the material remaining in the mother liquors yielded trans-1,2-cyclooctanediol as a viscous liquid that was characterized as the crystalline bis-phenylurethan. Both the cis- and trans-1,2-glycols were obtained more easily from cyclooctene.

Oxidation of cyclooctene with potassium permanganate, hydrogen peroxide and osmium tetroxide, and aqueous sodium chlorate and osmium tetroxide formed crystalline cis-1,2-cyclooctanediol in yields of 7.7, 11.4 and 30%, respectively. The cis configuration is assigned to the product because these methods of oxidation are known to form cis-glycols. cis-1,2-Cyclooctanediol was converted into a solid bis-phenylurethan with phenyl isocyanate, and a liquid isopropylidene derivative with acetone in the presence of anhydrous copper sulfate. Evidence for its structure was obtained by rapid quantitative reaction with periodic acid at room temperature, and by oxidation with alkaline permanganate forming suberic acid.

The hydroxylation of cyclooctene with performic acid ⁷

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- (7) D. Szwern, *Chem. Rev.*, 45, 1 (1949), lists the cases in which olefins have been converted into glycols with this reagent.
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was expected to form trans-1,2-cyclooctanediol. However, after alkaline hydrolysis of the monoformate, extraction and distillation yielded a mixture of products (71.5% calculated as cyclooctanediols) instead of the pure trans-1,2-glycol. Crystallization of the mixture was difficult, but it proved to be possible to separate trans-1,2-cyclooctanediol as the isopropylidene derivative,⁸ formed by treating the mixture with acetone

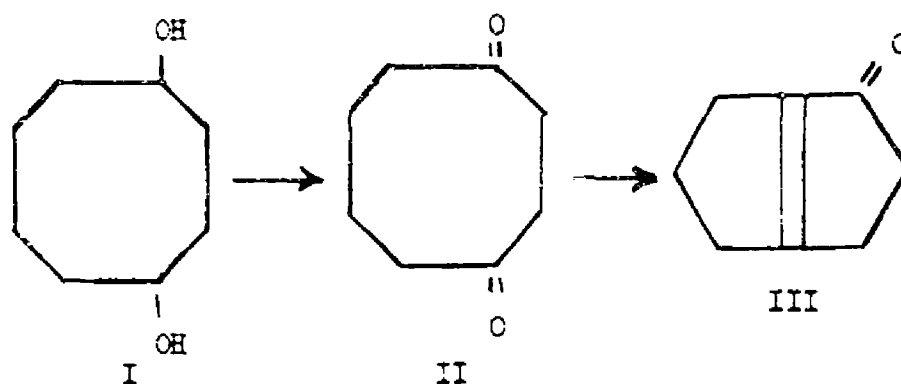
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- (8) Both cis- and trans-1,2-cycloheptanediols are known to form isopropylidene derivatives; J. Boeseken and H. Derx, *Rec. trav. chim.*, 40, 529 (1921); H. Derx, *ibid.*, 41, 312 (1922).
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and anhydrous copper sulfate. Subsequent distillation separated the more volatile isopropylidene derivative (30% or 21.5% based on cyclooctene) from a less volatile residue (described below). Acid hydrolysis of the isopropylidene derivative, or treatment with formic acid followed by basic hydrolysis of the formate, yielded trans-1,2-cyclooctanediol as a viscous liquid that was characterized as the crystalline bis-phenylurethan (identical with the derivative of the trans-1,2-glycol prepared from suberoin) and di-p-toluenesulfonate. trans-1,2-Cyclooctanediol, like the cis isomer, reacted rapidly and quantitatively with periodic acid at room temperature, and formed suberic acid on oxidation with alkaline permanganate.

The residue remaining after distilling the isopropylidene derivative of trans-1,2-cyclooctanediol from the mixture was crystallized from ethyl acetate, and yielded 36% (25.7% based on cyclooctene) of an isomeric glycol (I) that crystallized as fine needles, m.p. 85-86.5°. This glycol failed to react with periodic acid, showing that it probably was not a 1,2-glycol. Oxidation with aqueous sodium

permanganate yielded a mixture containing oxalic acid and adipic acid, indicating a chain of at least six carbon atoms separating the alcoholic hydroxyl groups. The bis-phenylurethan and di-p-toluenesulfonate were prepared from I as solid derivatives. Evidence concerning the carbon skeleton of I was obtained by converting the glycol to the diacetate, which was pyrolyzed at 500° and formed a mixture of cyclooctadienes that was reduced quantitatively to cyclooctane. Excluding the unlikely possibility that ring contraction during hydroxylation of cyclooctene might be followed by ring expansion in pyrolysis of the diacetate, this evidence is sufficient to establish the structure of I as a cyclooctane-diol other than the cis-or trans-1,2-diol.

Evidence concerning the orientation of the hydroxyl groups was obtained by oxidation of I by the Oppenauer method, which formed a diketone II that failed to give a ferric chloride enol test (expected to be positive for 1,3-cyclooctanedione). On treatment with dilute sodium hydroxide followed by hydrochloric acid, or directly with concentrated sulfuric acid, the diketone II underwent an intramolecular aldol condensation and formed the known unsaturated ketone, bicyclo [3.3.0]-1(5)-octen-2-one (III), which was isolated as the semicarbazone. Accordingly the diketone II is 1,4-cyclooctanedione, and the glycol from which it is formed is cis-or trans-1,4-cyclooctanediol (I).



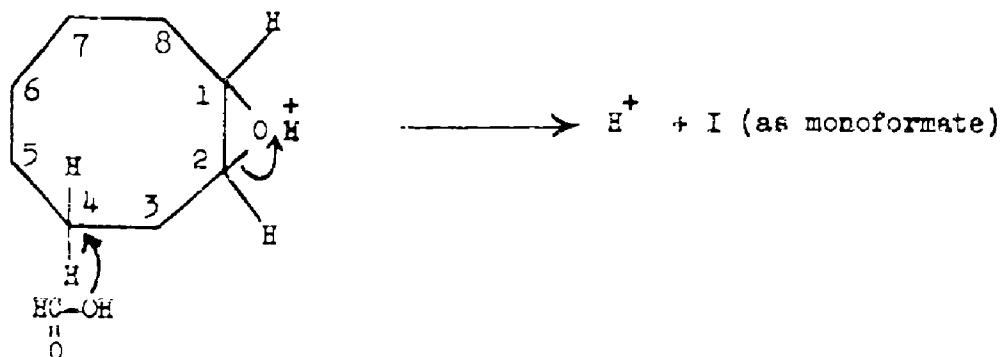
Since the formation of a 1,4-glycol by hydroxylation of an olefin with performic acid appeared to be without precedent, evidence was sought concerning the step in the process in which rearrangement occurred. Cyclooctane oxide was prepared from cyclooctene and peracetic acid, and purified by distillation and sublimation; m.p. 56-57°. Fractional distillation and chromatography on both alumina and activated carbon, followed by fractional elution with solvents, failed to separate fractions with significantly different melting points or infrared spectra, indicating that the epoxide was homogeneous. Cyclooctene oxide was hydrogenated to cyclooctanol in 83% yield in the presence of Raney nickel at 125°. This normal behavior on reduction provides evidence that the oxide is a normal 1,2-epoxide. The

solvolysis of cyclooctene oxide with formic acid, followed by saponification of the resulting formates, or hydrolysis of the oxide with dilute hydrochloric acid, formed a mixture of glycols similar to the mixture formed from cyclooctene and performic acid. trans-1,2-Cyclooctanediol was separated from the mixture as the isopropylidene acetal, after which 1,4-cyclooctanediol (I) was isolated from the residue by crystallization from ethyl acetate in 30% yield. Accordingly the step in which rearrangement occurs in the conversion of cyclooctene to 1,4-cyclooctanediol is the solvolysis of the epoxide.¹⁰

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- (10) Hydrolysis of cis-cyclooctene oxide to a liquid glycol presumed to be the trans-1,2-isomer has been reported by K. Ziegler and H. Wilms, *Ann.*, 567, 1 (1950), and M. Godchot and G. Cauquil, *Compt. rend.*, 192, 963 (1931), who report m.p. 182-183° and 166-167°, respectively, for the bis-phenylurethan. We have observed m.p. 176.2-177.4° for trans-1,2-cyclooctanediol bis-phenylurethan, and m.p. 186-187.5° for 1,4-cyclooctanediol bis-phenylurethan. Either of these derivatives or a mixture of them might have been isolated in the earlier work, if the glycol was a mixture of isomers similar to the one that we obtained.
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A tentative interpretation of the abnormal solvolysis of cyclooctene oxide is based on a hitherto unobserved chemical "transannular effect" for which the proximity of atoms lying across an eight-membered ring may be responsible. In other words, hydrogen atoms that are sterically adjacent to the oxide ring may participate in the displacement reaction in a kind of neighboring group effect for which the conformation of the ring is responsible. According to this

interpretation, the 1,4-glycol would be formed by a 1,3-hydride shift in the protonated epoxide, presumably occurring simultaneously with the attack by the solvent at the positively charged carbon in the 4-position, as formulated schematically below. Normal displacement at C₂ with Walden inversion would account for formation of the trans-1,2-glycol. Steric hindrance provided by the ring to approach of C₂ by the solvent might retard this "normal" displacement, allowing time for "abnormal" displacement at C₄.



A more exact interpretation must await determination of the configuration of I (cis or trans), and examination of the solvolysis products of cyclooctene oxide that have not been purified or identified ~~(about 28% of the total product)~~, and may contain products other than the trans-1,2 and 1,4-glycols. The solvolysis of epoxides of other

olefins also will be examined to determine whether glycols other than the expected 1,2-glycols are formed.¹¹

- (11) The fact that 1,4-cyclooctanediol is formed on hydroxylation of cyclooctane has been communicated to Professor V. Prelog, who has confirmed and extended this observation of a chemical "transannular effect" by studies of the hydroxylation of cyclodecane, to be published soon in *Helvetica Chimica Acta*.
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Experimental

- (12) Melting points are corrected and boiling points are uncorrected. We are indebted to Dr. S. M. Nagy and his associates for analyses.
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Suberoin. - A 5-l. three-necked flask was equipped with a mercury-sealed Herashberg stirrer and a simple high dilution apparatus,¹³ to which was attached a reflux condenser and a Herashberg

- (13) A. C. Cope and E. C. Herrick, *This Journal*, 72, 985 (1930).
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dropping funnel. Sodium (46 g., 2 g. atoms) was powdered by stirring under 1 l. of refluxing xylene, and a solution of 101 g. (0.5 mole) of dimethyl suberate (b.p. 111-112.5° at 2.3 mm., n_D^{28} 1.4303) in 80 ml. of xylene was added through the dilution apparatus over a period of 8 hours in an atmosphere of dry nitrogen, with stirring and refluxing¹⁴

- (14) The flask was heated with an oil bath. An electric heating mantle caused charring of the gelatinous sodium salt that separated as the reaction progressed.
-

during that period and for 2 hours longer. The mixture was allowed to stand overnight, and then was cooled with an ice bath. Absolute ethanol (50 ml.) was added to destroy any remaining sodium, followed by a solution of 120 g. (2 moles) of glacial acetic acid in 800 ml. of dry ether, added slowly with stirring to neutralize the mixture. The nitrogen atmosphere was maintained to this point. Sodium acetate was separated by filtration and washed well with ether, and the filtrate was concentrated under reduced pressure in a nitrogen atmosphere. The residue was distilled from a Hickman molecular-type pot still at 60-135° (0.5 mm.), and the distillate was fractionated through a 15 x 1-cm. Vigreux column under nitrogen, yielding 26 g. (37%) of suberoin, b.p. 66-71° (1.3 mm.). The nearly colorless product crystallized, and was purified by redistillation and crystallization from a mixture of ether and pentane; b.p. 64° (0.3 mm.), m.p. 37-38.5°.

Anal. Calcd. for $C_8H_{14}O_2$: C, 67.58; H, 9.92. Found:
C, 66.58; H, 9.95.

Preparation of cis and trans-1,2-Cyclooctanediols from Suberoin. A solution of 3.44 g. of suberoin in 75 ml. of methanol was shaken with hydrogen at room temperature and atmospheric pressure in the presence of 2.5 g. of W-7 Raney nickel catalyst.¹⁵ After 30 minutes,

(15) H. Adkins and H. R. Billica, This Journal, 70, 693 (1948).

95.3% of one molar equivalent of hydrogen had been absorbed and the

reduction stopped. The catalyst was separated by filtration, and the filtrate was concentrated under reduced pressure. The residue (3.48 g.) was a viscous liquid that partially crystallized. Several crystallizations of a sample (0.97 g.) from ethyl acetate yielded 0.37 g. of cis-1,2-cyclooctanediol as white leaflets, m.p. 77.5-79°, and 0.60 g. of a sirup. A solution of the sirup in 10 ml. of chloroform-carbon tetrachloride (2:1 by volume) was placed on a 13.5 x 1.5-cm. column of 48-100 mesh activated alumina, and the column was eluted with 200-ml. portions of the following solvents, from which the indicated weights of liquid residues were obtained: (1) chloroform-carbon tetrachloride (2:1), 0.06 g., (2) chloroform, 0.19 g.; (3) chloroform-methanol (9:1), 0.34 g. Fractions 2 and 3 were treated with phenyl isocyanate, and both yielded the bis-phenylurethan of trans-1,2-cyclooctanediol, m.p. 176.5-178.5° after crystallization from ethanol. The derivative gave no depression in mixed melting point with the bis-phenylurethan of trans-1,2-cyclooctanediol prepared from cyclooctene (described below), while a mixed melting point with the bis-phenylurethan of cis-1,2-cyclooctanediol (also described below) was depressed to 154-172°.

cis-1,2-Cyclooctanediol. - (a) A solution of 11.0 g. of cyclooctene (n_D^{25} 1.4681, prepared by partial hydrogenation of cyclooctatetraene^{4,5}) in 50 ml. of acetone was cooled to -20°, and a solution of 15.8 g. of potassium permanganate in 1.5 l. of acetone was added slowly with stirring at -20 to 0° over a period of 12 hours, at a rate

at which permanganate did not accumulate in the solution. The manganese dioxide was reduced by addition of saturated aqueous sodium bisulfite with stirring, and most of the acetone was removed by distillation. The residue was poured into 1500 ml. of water, and the solution was made alkaline with sodium carbonate and extracted with six 100-ml. portions of ether. The ether solution was dried over magnesium sulfate and distilled, and yielded 5.0 g. (45%) of recovered cyclooctene.¹⁶ A short path distillation of the residue at 1 mm. yielded 0.96 g. of cis-1,2-cyclooctanediol.¹⁶ The aqueous alkaline solution was acidified and extracted with eight 100-ml. portions of ether. Short path distillation of the residue obtained by concentrating the extracts yielded an additional 0.16 g. of the cis-1,2-diol, making the total yield 1.12 g. (7.7%); after recrystallization from ethyl acetate the cis-1,2-cyclooctanediol melted at 76-79°. Recrystallization from water of the dark solid residue remaining after the second short path distillation yielded 1.84 g. (10.6%) of suberic acid.

(b) Using the method described by Miles and Susman¹⁶ for

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- (16) H. A. Miles and S. Susman, This Journal, 59, 2547 (1937). In a model experiment cis-1,2-cyclohexanediol was obtained from cyclohexene in 51% yield under these conditions.
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the preparation of cis-1,2-cyclohexanediol, 15.1 g. of cyclooctene¹⁶ was added to 100 ml. of t-butyl alcohol containing 5.1 g. (0.15 mole) of hydrogen peroxide and cooled to -5°. Osmium tetroxide (3 ml. of a 0.5% solution in t-butyl alcohol) was added, and the solution was allowed

to stand for 42 hours at 0 to 5°. The product, isolated by the procedure described above, amounted to 2.24 g. (11.4%) of cis-1,2-cyclooctanediol and 0.75 g. of suberic acid. An analytical sample of cis-1,2-cyclooctanediol was prepared by recrystallization from ethyl acetate; m.p. 77.5-79°.

Anal. Calcd. for $C_8H_{16}O_2$: C, 66.62; H, 11.18. Found: C, 66.81; H, 11.04.

(c) A mixture of 11.0 g. of cyclooctene, 7.6 g. of sodium chlorate, 5 ml. of acetic acid, 50 ml. of water, 100 ml. of dioxane and 5 ml. of 1% osmium tetroxide in t-butyl alcohol was heated under reflux for 72 hours.¹⁷ The solution was concentrated

(17) A hydroxylation procedure similar to one used for hydroxylation of maleic and fumaric acid by M. Zelikoff and H. A. Taylor, This Journal, 72, 5039 (1950).

under reduced pressure, and the residue was distilled in a short path still. A low boiling fraction of 1.3 g. distilling at a block temperature of 80-100° (0.3 mm.) was separated, followed by 8.6 g. of crude cis-1,2-cyclooctanediol, collected at 120-150° (0.3 mm.). Recrystallization from ethyl acetate yielded 4.3 g. (30%) of cis-1,2-cyclooctanediol, m.p. 75.8-78°.

cis-1,2-Cyclooctanediol was characterized by oxidation with alkaline permanganate to suberic acid, by rapid oxidation with periodic acid at 25°, which proceeded to the extent of 98.2% within

30 minutes, and by preparation of the following derivatives.

cis-1,2-Cyclooctanediol bis-Phenylurethan was prepared

by treating the cis-glycol with phenyl isocyanate without solvent for 44 hours at room temperature. The crude product was washed with hexane and recrystallized from ethanol; m.p. 175.5-176.8°.

Anal. Calcd. for $C_{22}H_{28}N_2O_4$: C, 69.09; H, 6.85.

Found: C, 69.24; H, 6.87.

cis-1,2-Cyclooctanediol Isopropylidene Ketal was prepared

by shaking a solution of 1.44 g. of the cis-glycol in 25 ml. of dry acetone with 5.0 g. of anhydrous copper sulfate at room temperature for 43 hours.¹⁸ The mixture was filtered, concentrated, and the residue

(18) Based on a procedure for preparing isopropylidene derivatives of 1,2-glycols described by C. Niemann and C. D. Wagner, J. Org. Chem., 7, 230 (1942).

was distilled through a semimicro column.¹⁹ The yield of cis-1,2-cyclo-

(19) C. W. Gould, Jr., G. Holzman and C. Niemann, Anal. Chem., 20, 361 (1948).

octane₂diol isopropylidene ketal was 1.23 g. (67%), b.p. 97-98° (10 mm.),
²⁵
 n_D 1.4600.

Anal. Calcd. for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94.

Found: C, 71.52; H, 10.97.

Performic Acid Oxidation of Cyclooctene. - A procedure

described for the oxidation of cyclohexene to trans-1,2-cyclohexanediol²⁰

(20) A. Reabuck and H. Adkins, Org. Syntheses, 28, 35 (1948).

was used, except that the product (after basic hydrolysis of the mono-formate) was extracted with four 100-ml. and three 50-ml. portions of chloroform. The product obtained from 55.2 g. of cyclooctene, 60 ml. of commercial 35% hydrogen peroxide and 300 ml. of 87% formic acid was distilled without any attempt at fractionation and amounted to 51.5 g. (corresponding to 71.5% of cyclooctanediols) of a very viscous liquid, b.p. 97-125° (0.2-0.5 mm.).

trans-1,2-Cyclooctanediol Isopropylidene Ketal was prepared

by shaking a solution of 28.4 g. of the above mixture in 300 ml. of dry acetone with 30 g. of anhydrous copper sulfate at room temperature for 22 hours. The mixture was filtered, the filtrate was concentrated, and the residue was distilled through a semimicro column, yielding 11.0 g. (30% from the crude mixture of glycols) of trans-1,2-cyclooctanediol isopropylidene ketal, b.p. 66.5-67° (1.3 mm.), n_D^{25} 1.4585.

Anal. Calcd. for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94.

Found: C, 71.44; H, 10.68.

1,4-Cyclooctanediol was isolated from the distillation residue, which was dissolved in 25 ml. of ethyl acetate and cooled to 0°. The colorless, crystalline 1,4-diol that separated was recrystallized from ethyl acetate and obtained in a yield of 10.3 g. (36% from the crude mixture of glycols) as fine needles, m.p. 85-86.5°; mixed melting point with cis-1,2-cyclooctanediol, 53-65°. Evidence for the structure of the 1,4-diol is presented below.

Anal. Calcd. for $C_8H_{16}O_2$: C, 66.62; H, 11.18. Found:
C, 66.72; H, 11.11.

A semisolid mixture (8 g. or 28% of the crude mixture
calculated as $C_8H_{16}O_2$)
obtained by concentration of the ethyl acetate mother liquors and
short path distillation of the residue at 0.35 mm. with a heating
block temperature of 100-133°, is being examined further to determine
whether it contains other isomeric cyclooctanediols.

trans-1,2-Cyclooctanediol was obtained by heating a
2.0 g. sample of the isopropylidene ketal with 10 ml. of 85% formic
acid for 2 hours at 100°, concentrating the solution, and shaking the
residue with 15 ml. of 20% aqueous sodium hydroxide for 30 minutes.
The product was extracted with 25 ml. of chloroform, and the extract
was dried over magnesium sulfate. The solution was concentrated and
the residue was distilled through a semimicro column, yielding 1.4 g.
(89%) of trans-1,2-cyclooctanediol as a viscous, colorless liquid
that failed to crystallize; b.p. 93-94° (0.5 mm.), n_D^{25} 1.4980.

Anal. Calcd. for $C_8H_{16}O_2$: C, 66.62; H, 11.18.

Found: C, 66.90; H, 11.35.

Hydrolysis of a 5.7 g. sample of the isopropylidene ketal
by heating under reflux for four hours with 100 ml. of water containing
a few drops of hydrochloric acid was incomplete; 2.7 g. of the ketal
steam distilled on concentrating the solution and was recovered from
the distillate. trans-1,2-Cyclooctanediol (1.7 g.) was extracted from

the aqueous residue with chloroform and distilled as described above. Another sample of trans-1,2-cyclooctanediol with the same physical properties was obtained by saponification of 0.56 g. of the bis-phenylurethan (described below) by heating under reflux with 25 ml. of 20% alcoholic potassium hydroxide for 23 hours.

trans-1,2-Cyclooctanediol was characterized by oxidation to suberic acid with alkaline permanganate, oxidation with periodic acid at 25°, which was complete within 20 minutes with reduction of 99.9% of the calculated quantity of the oxidizing agent, and by preparation of the bis-phenylurethan.

trans-1,2-Cyclooctanediol bis-Phenylurethan was prepared by warming the trans-1,2-diol briefly with phenyl isocyanate and allowing the mixture to stand overnight. The crude solid product was washed with hexane and recrystallized from ethanol; m.p. 176.2-177.4°, and mixed m.p. with cis-1,2-cyclooctanediol bis-phenylurethan, 154-163°.

Anal. Calcd. for $C_{22}H_{32}N_2O_4$: C, 69.09; H, 6.85.

Found: C, 69.16; H, 7.12.

Cyclooctene Oxide. - Commercial 40% peracetic acid ²¹

(21) Obtained from the Becco Sales Corporation, Buffalo, New York.

(125 ml.), to which 25 g. of sodium acetate trihydrate had been added to neutralize the sulfuric acid present, was added dropwise during 45

minutes with vigorous stirring to 55 g. of cyclooctene. The reaction temperature was maintained at 27-29° with an ice bath. The mixture was cooled to 0°, neutralized with 40% sodium hydroxide, and extracted with three 200-ml. portions of ether. The extracts were dried over magnesium sulfate, concentrated, and the residue was distilled through a 20 x 1.8-cm. column packed with glass helices. The yield of cyclooctene oxide, b.p. 90-93° (37 mm.), m.p. 52.5-56.5°, was 54.2 g. (86%). Cyclooctene oxide was purified by sublimation under reduced pressure as needles melting at 56-57°, with a very characteristic odor. Homogeneity of the epoxide was established by chromatography on alumina and on activated carbon followed by fractional elution with pentane-ether, and also by fractional distillation. Comparison of the melting points and infrared spectra of the various fractions showed no significant differences.

Hydrogenation of a solution of 5.0 g. of cyclooctene oxide in 5 ml. of ethanol at 125° in the presence of 0.5 g. of Raney nickel at 1900-1500 p.s.i. was complete in 1 hour, and yielded 4.24 g. (83%) of cyclooctanol, b.p. 92-93° (12 mm.), n_D^{25} 1.4842, m.p. 24.3-24.5°, identified by its infrared spectrum and by oxidation to cyclooctanone with chromic acid.

Solvolysis of Cyclooctene Oxide with Formic Acid. - A mixture of 5.03 g. of cyclooctene oxide and 25 ml. of 85% formic acid was heated under reflux for 30 minutes. The excess formic acid was re-

moved under reduced pressure, and the viscous residue was shaken with 50 ml. of 10% sodium hydroxide for 1 hour. The product was extracted with chloroform, and the extract was dried over magnesium sulfate and concentrated. The residue was distilled and yielded 4.6 g. of a mixture of cyclooctanediols, b.p. 120-130° (0.18 mm.), which was separated by the procedure described above for the mixture obtained by oxidation of cyclooctene with performic acid. The yield of trans-1,2-cyclooctanediol isopropylidene ketal was 1.42 g. (19%), b.p. 60-62° (1.1 mm.), n_D^{25} 1.4584. The residue remaining after distillation of the ketal was crystallized from ethyl acetate and yielded 1.7 g. (30%) of 1,4-cyclooctanediol, m.p. 84.6-86.2°. Any other isomeric cyclooctanediols that may have been present in the crystallization mother liquors were not isolated.

The same products were formed by hydrolysis of cyclooctene oxide with boiling 1% hydrochloric acid, and were isolated in the manner described above.

Structure of 1,4-Cyclooctanediol. - 1,4-Cyclooctanediol, m.p. 85-86.5°, prepared by performic acid oxidation of cyclooctene or by solvolysis of cyclooctene oxide with formic acid, failed to react at all with periodic acid during 24 hours under conditions that resulted in quantitative oxidation of cis- and trans-1,2-cyclooctanediols in 20 to 30 minutes. A solution of 0.72 g. of the 1,4-diol in 15 ml. of water was oxidized by addition of 2.0 g. of sodium permanganate tri-

hydrate as a 2% aqueous solution with stirring over a period of 45 minutes at 0-20°. The excess permanganate and manganese dioxide were reduced with sulfur dioxide at 0°, and the solution was acidified with hydrochloric acid and extracted continuously with ether for 14 hours. A mixture of acids (0.83 g.) remained as a residue after distillation of the ether, and was separated into two fractions by sublimation under reduced pressure: (1) oxalic acid, 0.20 g., m.p. 186-189° (dec.), and m.p. and mixed m.p. with oxalic acid hydrate 99-100° after recrystallization from water; (2) adipic acid, recrystallized from water, 0.41 g., m.p. and mixed m.p. with an authentic sample 152-153°.

1,4-Cyclooctanediol bis-Phenylurethan was prepared by warming the 1,4-diol with a slight excess of phenyl isocyanate for a short time and allowing the mixture to stand overnight. The solid product was washed with petroleum ether and recrystallized from benzene and from ethanol; m.p. 186-187.5°; mixed m.p. with cis-1,2-cyclooctanediol bis-phenylurethan, 154-172°; mixed m.p. with trans-1,2-cyclooctanediol bis-phenylurethan, 159-180°.

Anal. Calcd. for $C_{22}H_{32}N_2O_4$: C, 69.09; H, 6.85; mol. wt., 382. Found: C, 69.01; H, 7.11; mol. wt., 354 (Rast method in camphor).

1,4-Cyclooctanediol 11-p-toluenesulfonate was prepared by adding 3.6 g. of p-toluenesulfonyl chloride with cooling to a solution of 1.25 g. of the 1,4-diol in 10 ml. of dry pyridine. The mixture was allowed to stand at room temperature overnight, and poured into 75 ml. of ice 3 N hydrochloric acid. The product was extracted with three 75-ml. portions of ether, which were combined, dried over magnesium sulfate, and concentrated under reduced pressure. The colorless liquid residue (3.66 g.) was crystallized from methanol, and yielded 2.83 g. (72%) of the di-tosylate as colorless needles, which after recrystallization from methanol melted at 96.5-98.5° (dec., introduced at 94°).

Anal. Calcd. for $C_{22}H_{28}O_8S_2$: C, 58.38; H, 6.24.

Found: C, 58.47; H, 6.27.

1,4-Cyclooctanediol Diacetate was prepared by heating 2.61 g. of the 1,4-diol and 2.5 g. of anhydrous sodium acetate with 6 ml. of acetic anhydride at 50° for 3 hours. The mixture was poured onto ice, neutralized with saturated sodium bicarbonate solution, and the product was extracted with 50 ml. of ether. The extract was dried over magnesium sulfate, concentrated, and the residue was distilled in a short path still at 0.07 mm. with a heating block temperature of 100°; yield 4.08 g. (95%), n_D^{25} 1.4631.

Anal. Calcd. for $C_{18}H_{26}O_4$: C, 63.13; H, 8.83. Found:

C, 63.38; H, 8.83.

A 3.78-g. sample of the diacetate was pyrolyzed at 500° in a slow stream of nitrogen by introduction over a period of 1.5 hours into a vertically mounted tube containing a 50 x 1.0-cm. heated section packed with glass helices. The condensate that was collected in a trap cooled with Dry Ice was washed with sodium bicarbonate solution and extracted with pentane. The solution was dried over sodium sulfate, concentrated, and the residue was distilled through a semimicro column, yielding 1.46 g. (81%) of a mixture of cyclooctadienes, n_D^{25} 1.4895-1.4930. A fraction with n_D^{25} 1.4922 was analyzed.

Anal. Calcd. for C_8H_{12} : C, 88.81; H, 11.19. Found: C, 89.11; H, 11.28.

Hydrogenation of a solution of 0.520 g. of the mixture of dienes in 7 ml. of acetic acid in the presence of 0.1 g. of pre-reduced platinum oxide was complete in 3 hours and 95% of two molar equivalents of hydrogen was absorbed. The product was isolated by a procedure described previously²² and amounted to 0.491 g. (91%)

(22) A. C. Cope and F. A. Hochstein, This Journal, 72, 2517 (1950).

of cyclooctane, b.p. 73-74° (90 mm.), n_D^{25} 1.4557, m.p. 8-9.5° (indicating 98% purity) and mixed m.p. with an authentic sample, 9.5-10.4°. The sample of cyclooctane was also identified by its infrared spectrum.

1,4-Cyclooctanedione was obtained by heating a mixture

of 7.2 g. of 1,4-cyclooctanediol, 10.8 g. of p-benzoquinone, 1.0 g. of aluminum isopropoxide and 250 ml. of toluene under reflux for 14 hours. The mixture was cooled, filtered to separate hydroquinone, concentrated, and the residue was distilled in a short path still at 0.05 mm. with a bath temperature of 60-175°. The distillate was collected in a receiver cooled with Dry Ice, and fractionated through a semimicro column. The yield of 1,4-cyclooctanedione, b.p. 75-75.5° (1 mm.), was 1.08 g. (15%). The diketone gave a negative encl test with ferric chloride.

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.82; H, 8.94.

The 1,4-cyclooctanedione derived from the 1,4-diol was characterized by conversion into the known semicarbazone of bicyclo [3.3.0]-1(5)-octen-2-one.²³ A 70-mg. sample of the diketone was added

(23) A. C. Cope and W. R. Schmitz, *ibid.*, 72, 3059 (1950).

to 2% aqueous sodium hydroxide, and allowed to stand at 26° for 8 hours. The dark mixture was extracted with three 20-ml. portions of ether, and the extracts were concentrated. The residue was treated with 15 ml. of 10% hydrochloric acid for 1 hour at room temperature and 3 hours at 70°. The mixture was neutralized with sodium bicarbonate and steam distilled. To the distillate (200 ml.) was added 0.1 g. of semicarbazide hydrochloride and 0.15 g. of sodium acetate trihydrate. The mixture was

heated on a steam bath for 20 minutes and cooled to 0° overnight and the crystalline bicyclo[3.3.0]-1(5)-octen-2-one semicarbazone was separated and recrystallized from aqueous ethanol; m.p. and mixed m.p. with an authentic sample, 237-238.5° (dec.). Infrared spectra of Nujol mulls of the two semicarbazone samples were identical within experimental error.

A 140-mg. sample of 1,4-cyclooctanediⁿone was treated with 0.3 ml. of concentrated sulfuric acid at 0° for 1 hour and 70° for 20 minutes, after which the mixture was neutralized, steam distilled, and bicyclo[3.3.0]-1(5)-octen-2-one semicarbazone was isolated from the distillate (20 ml.) by the procedure described above in a yield of 87 mg. (48%).

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